

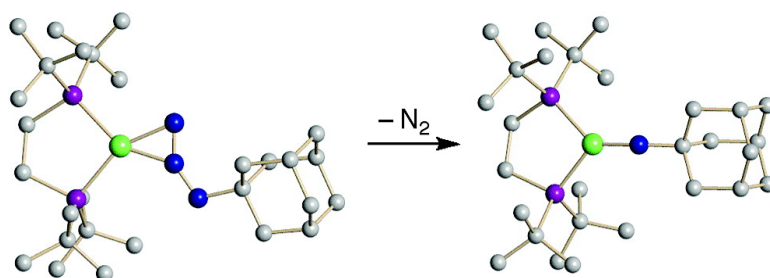
Communication

**#-Organoazide Complexes of Nickel and Their Conversion to Terminal Imido Complexes via Dinitrogen Extrusion**

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## $\eta^2$ -Organoazide Complexes of Nickel and Their Conversion to Terminal Imido Complexes *via* Dinitrogen Extrusion

Rory Waterman<sup>†</sup> and Gregory L. Hillhouse\*

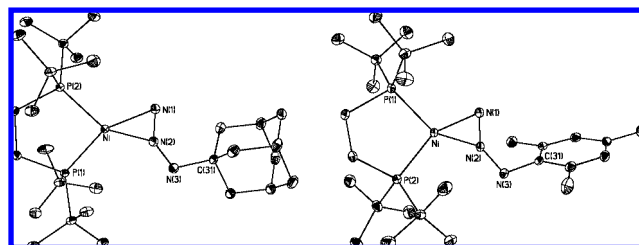
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Our reports of the syntheses and structures of the three-coordinate nickel imido, carbene, and phosphinidene complexes (dtbpe)Ni=N(2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**1**; dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane),<sup>1</sup> (dtbpe)Ni=CPh<sub>2</sub>,<sup>2</sup> and (dtbpe)Ni=P(2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sup>3</sup> initiated ongoing studies of rich group-transfer reaction chemistries of these Ni=X multiply bonded species.<sup>2,4</sup> Imido complex **1** is best prepared by 1-e<sup>-</sup> oxidation of the Ni(I) amido complex (dtbpe)Ni{NH(2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)} followed by deprotonation of the resulting cationic Ni(II) amide (dtbpe)Ni{NH(2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)}<sup>+</sup>.<sup>1</sup> In search of a simplified and general preparation of (dtbpe)Ni=NR complexes, we have investigated the reactions of organoazides with Pörschke's labile Ni(0) benzene complex {(dtbpe)Ni}<sub>2</sub>( $\eta^2$ - $\mu$ -C<sub>6</sub>H<sub>6</sub>) (**2**).<sup>5</sup> Organoazides have long been recognized as useful synthons for early transition metal imido moieties.<sup>6</sup> For late metals, Warren has reported the syntheses of Ni(III) imido complexes from the reaction of RN<sub>3</sub> with [Me<sub>2</sub>C<sub>3</sub>H(NMes)<sub>2</sub>]Ni(2,4-lutidine),<sup>7</sup> and Peters and Theopold have applied this strategy to Co systems.<sup>8,9</sup> This approach seemed particularly attractive in our system in light of the observation that the  $\eta^2$ -diphenyldiazomethane adduct (dtbpe)Ni( $\eta^2$ -N<sub>2</sub>CPh<sub>2</sub>), prepared from N<sub>2</sub>CPh<sub>2</sub> and a suitable Ni(0) precursor, cleanly converts to (dtbpe)Ni=CPh<sub>2</sub> upon thermolysis in the presence of catalytic Sm(OTf)<sub>3</sub>.<sup>2</sup>

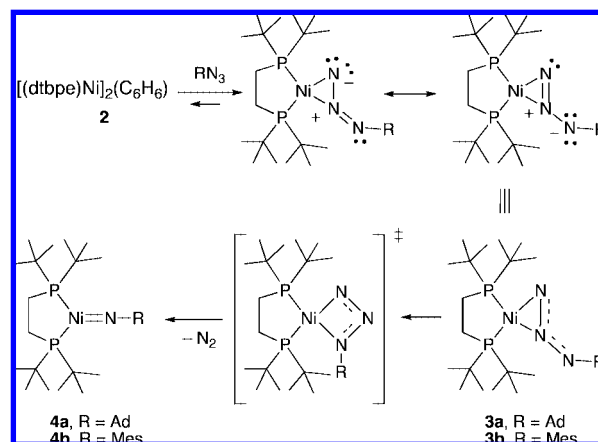
Reaction of hexane solutions of **2** with 1-azidoadamantane affords the unusual 1-adamantylazide adduct (dtbpe)Ni( $\eta^2$ -N<sub>3</sub>Ad) (**3a**, Ad = 1-adamantyl) as analytically pure, golden crystals in 76% isolated yield (Scheme 1). Mesitylazide reacts in an analogous fashion with **2** in a dilute toluene solution to give (dtbpe)Ni( $\eta^2$ -N<sub>3</sub>Mes) (**3b**) as yellow crystals in 64% isolated yield, but this complex is somewhat thermally unstable, slowly decomposing at ambient temperature even in the solid state. <sup>1</sup>H and <sup>31</sup>P NMR spectra of **3a** and **3b** demonstrate the C<sub>s</sub>-symmetry of the complexes (inequivalent <sup>31</sup>P nuclei with pairwise-inequivalent *tert*-butyl groups). Addition of MesN<sub>3</sub> to C<sub>6</sub>D<sub>6</sub> solutions of **3a** results in formation of **3b** and AdN<sub>3</sub>, suggesting the RN<sub>3</sub> ligand is labile in that solvent (Scheme 1).

The  $\eta^2$ -coordination of the N<sub>3</sub>R ligands in **3a** and **3b** was confirmed by X-ray crystallography. The solid-state structures are shown in Figure 1 and feature planar geometry at nickel and delocalized  $\pi$ -bonding in the N<sub>3</sub> framework (for **3a**, N(1)–N(2) = 1.244(2), N(2)–N(3) = 1.298(3) Å). This is a unique coordination mode for organoazide ligands and is similar to the  $\eta^2$ -coordination observed for diazoalkane and diazonium complexes of the (dtbpe)Ni fragment.<sup>2,10</sup> Cummins has reported a structurally related  $\eta^2$ -P<sub>2</sub>NR complex of niobium.<sup>11</sup> In the few instances where a metal complex bears an organic azide, the ligand is bound as a diazenylimido (RN<sub>3</sub><sup>2-</sup> as **A**, **B**, **C**; Chart 1)<sup>12–15</sup> or  $\eta^1$  as neutral RN<sub>3</sub> through either the  $\alpha$  or  $\gamma$  N-atoms (**D**, **E**).<sup>16–18</sup>  $\eta^6$ -Aryl azide coordination

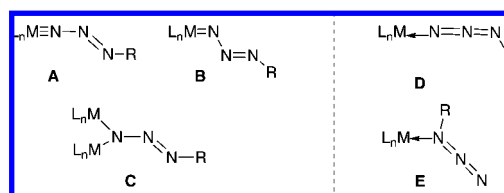


**Figure 1.** Structures of **3a** (l) and **3b** (r) with thermal ellipsoids at 35% probability and H-atoms omitted. Select bond lengths (Å) and angles (deg) for **3a**: Ni–N(1) = 1.910(2), Ni–N(2) = 1.810(2), N(1)–N(2) = 1.244(2), N(2)–N(3) = 1.298(3), N(3)–C(31) = 1.484(3). P(1)–Ni–P(2) = 93.75(2), P(1)–Ni–N(2) = 114.60(6), P(2)–Ni–N(1) = 112.72(6), N(1)–Ni–N(2) = 38.97(8), N(1)–N(2)–N(3) = 142.7(2), N(2)–N(3)–C(31) = 113.6(2). For **3b**: Ni–N(1) = 1.906(2), Ni–N(2) = 1.811(2), N(1)–N(2) = 1.239(3), N(2)–N(3) = 1.308(3), N(3)–C(31) = 1.438(3). P(1)–Ni–P(2) = 92.90(3), P(2)–Ni–N(2) = 115.61(7), P(1)–Ni–N(1) = 112.84(7), N(1)–Ni–N(2) = 38.85(9), N(1)–N(2)–N(3) = 138.7(2), N(2)–N(3)–C(31) = 112.8(2).

### Scheme 1



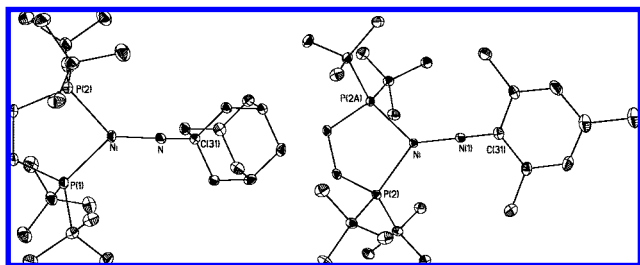
### Chart 1



through the aromatic ring is known for  $[(\eta^6\text{-ArN}_3)\text{Mn}(\text{CO})_3]^+[\text{PF}_6]^-$  (Ar = Ph, *p*-Tol).<sup>19</sup>

Thermolysis of benzene solutions of either pure **3a** or **3b** yields myriad products. However, heating benzene solutions of pure **3a** with a substoichiometric amount of **2** (~5 mol %) gives analytically

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**Figure 2.** Perspective views of **4a** (l) and **4b** (r) with thermal ellipsoids drawn at 35% probability and H-atoms omitted. Select bond lengths (Å) and angles (deg) for **4a**: Ni–N = 1.673(2), N–C(31) = 1.417(3), Ni–P(1) = 2.1371(8), Ni–P(2) = 2.1405(8), Ni–N–C(31) = 163.0(2), P(1)–Ni–P(2) = 91.69(3). For **4b**: Ni–N(1) = 1.703(4), N–C(31) = 1.347(7), Ni–P(2) = 2.179(1), Ni–N–C(31) = 180, P(1)–Ni–P(2) = 91.12(5).

pure dark red crystals of (dtbpe)Ni=NAd (**4a**) in 81% yield (Scheme 1). The beneficial role of added **2** appears to be to keep the equilibrium concentration of free AdN<sub>3</sub> low (favoring **3a** in the equilibrium shown in Scheme 1). We have shown that AdN<sub>3</sub> undergoes a side reaction with **4a** to effect its decomposition (forming azoadamantane, AdN=NAd).<sup>20</sup> The terminal mesityl imido complex (dtbpe)Ni=NMe (**4b**) can be similarly prepared, but the best yields are obtained by treatment of concentrated petroleum ether solutions of **2** with MesN<sub>3</sub> to afford **4b** in 84% yield as analytically pure turquoise crystals. <sup>1</sup>H and <sup>31</sup>P NMR spectra of complexes **4a** and **4b** are consistent with pseudo C<sub>2v</sub>-symmetry and present features typical of a terminal imido complex of nickel(II).<sup>1</sup> Both imido complexes **4a** and **4b** were crystallographically characterized (Figure 2). These complexes and previously reported imido **1** highlight interesting structural features associated with the nitrogen substituent. The metrical parameters of **4b** and **1** are nearly identical except that the Ni–N–C angle is rigorously linear for **4b** while it is slightly bent at 162.8(2)° in **1**. The alkylimido **4a** has a Ni–N–C angle (163.0(2)°) similar to that for **1** with a slightly shorter Ni–N bond ( $\Delta \sim 0.03$  Å).<sup>1</sup>

Kinetic studies of the conversion of **3a** to **4a** were undertaken to provide insight into this process. Because of the lability of the azide ligand in **3a** in benzene solution (*vide supra*), kinetic measurements were carried out in the presence of  $\sim 5$  mol% of **2**, although the rate was shown to be independent of [**2**]. The conversion of **3a** to **4a** as measured by <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>) shows first-order dependence on [**3a**] with  $k_{\text{obs}} = 1.70(8) \times 10^{-3} \text{ s}^{-1}$  at 45 °C ([**3a**]<sub>0</sub> =  $6.1 \times 10^{-2}$  M). An Eyring analysis of the temperature dependence of the rate over a 23–70 °C range yielded activation parameters ( $\Delta H^\ddagger = 15.9(7) \text{ kcal/mol}$ ;  $\Delta S^\ddagger = -19.7(9) \text{ eu}$ ) suggestive of a highly ordered transition state. A four-membered cyclic transition state, involving RN<sub>3</sub> coordination to Ni through both the  $\alpha$ - and  $\gamma$ -nitrogen atoms prior to N<sub>2</sub> loss (Scheme 1), is consistent with these data and is similar to one proposed by Bergman in the thermal decomposition of Cp<sub>2</sub>TaMe( $\eta^1$ -N<sub>3</sub>-*p*-Tol)<sup>12</sup> (rather than trapping of a triplet nitrene fragment).<sup>21</sup>

In summary, we have demonstrated that that alkyl- and aryl-substituted nickel(II) imido complexes can be prepared directly from organic azides and an appropriate Ni(0) precursor. This method complements the previously reported route to Ni(II) imides that relies on sequential preparation of a Ni(I) amide followed by its chemical oxidation to a cationic Ni(II) amide that can be deprotonated to afford the Ni(II) imide. In principle this route offers the possibility for carrying out catalytic “nitrene-transfer” reactions to

olefins (aziridination) with RN<sub>3</sub> using **2** as a catalyst precursor. Such group-transfer reactions are by nature restricted to being stoichiometric ones when a multistep synthetic protocol involving Ni(I) is required to access the key L<sub>2</sub>Ni=NR complexes.<sup>4a,22</sup> Two features of this system, however, appear to obviate its development into a functional catalytic process. First, the success of the conversion of **2** to **4** relies on having a sufficiently labile ligand, like  $\eta^2$ -C<sub>6</sub>H<sub>6</sub>, in the Ni(0) precursor complex. Common olefins (e.g., ethylene, 1-hexene, 1,5-cyclooctadiene) bind too strongly to the (dtbpe)Ni-fragment and are not displaced by RN<sub>3</sub> to give  $\eta^2$ -N<sub>3</sub>R complexes. Second, the reaction of RN<sub>3</sub> with **4** to give RN=NR is faster at reasonable N<sub>3</sub>R concentrations than is the aziridination of olefins by **1**.<sup>4a,20</sup> It is noteworthy that these limiting factors can be overcome in the related cyclopropanation of ethylene by N<sub>2</sub>CPh<sub>2</sub>, where modest catalytic turnover is observed using (dtbpe)Ni=CPh<sub>2</sub>.<sup>4a</sup>

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**Supporting Information Available:** Experimental procedures with characterization data and kinetic data (PDF) as well as crystallographic information for **3a**, **3b**, **4a**, and **4b** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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